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Alpha-Dicarbonyl Yields from the NOx-Air Photooxidations of a Series of Aromatic Hydrocarbons in Air

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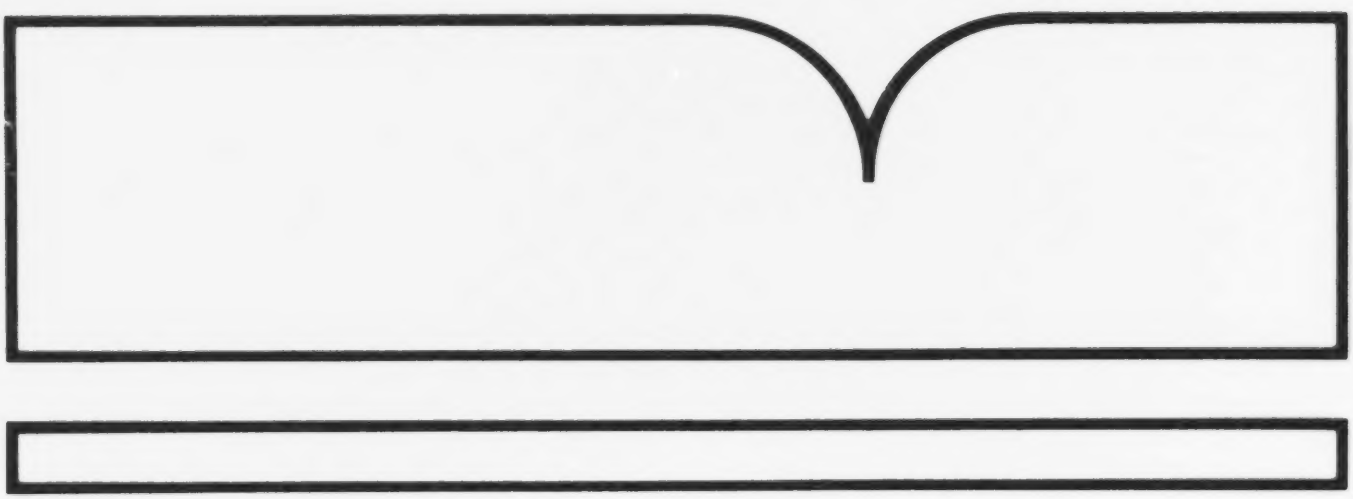

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16. ABSTRACT

The yields of the ring cleavage products glyoxal, methylglyoxal and biacetyl from the reactions of OH radicals with benzene, toluene, o-, m- and p-xylene and 1,2,3-, 1,2,4- and 1,3,5-trimethylbenzene in the presence of part-per-million concentrations of NO have been determined in one atmosphere of air using in situ long pathlength Fourier transform infrared absorption spectroscopy and differential optical absorption spectroscopy with supplementary gas chromatographic analyses. The yields of glyoxal and methylglyoxal were respectively: from toluene, 0.105 ± 0.019 and 0.146 ± 0.006; from o-xylene, 0.087 ± 0.012 and 0.246 ± 0.020; from m-xylene, 0.086 ± 0.011 and 0.319 ± 0.009; from p-xylene, 0.225 ± 0.039 and 0.105 ± 0.034; from 1,2,3-trimethylbenzene, 0.058 ± 0.008 and 0.152 ± 0.025; and from 1,2,4-trimethylbenzene, 0.048 ± 0.005 and 0.357 ± 0.017. In addition, a glyoxal yeild from benzene of 0.207 ± 0.019, a methylglyoxal yield from 1,3,5-trimethylbenzene of 0.602 ± 0.033, and biacetyl yields from 1,2,3- and 1,2,4-trimethylbenzene of 0.316 ± 0.036 and 0.048 ± 0.009, respectively, were determined. These data are important inputs to chemical models of the NO_x-air photooxidations of these aromatic hydrocarbons.

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α-Dicarbonyl Yields from the NO_x–Air Photooxidations of a Series of Aromatic Hydrocarbons in Air

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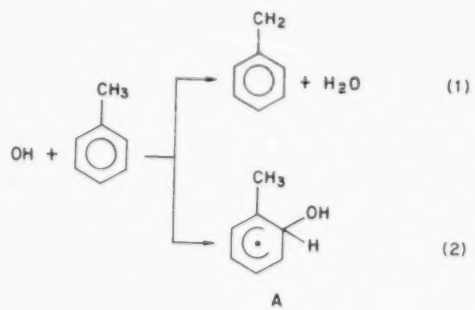
■ The yields of the ring cleavage products glyoxal, methylglyoxal, and biacetyl from the reactions of OH radicals with benzene, toluene, *o*-, *m*-, and *p*-xylene, and 1,2,3-, 1,2,4-, and 1,3,5-trimethylbenzene in the presence of parts per million concentrations of NO have been determined in 1 atm of air at 298 ± 2 K using in situ long-path-length Fourier transform infrared absorption spectroscopy and differential optical absorption spectroscopy with supplementary gas chromatographic analyses. The yields of glyoxal and methylglyoxal, after correction for their photolysis and reaction with OH radicals, were, respectively, as follows: from toluene, 0.105 ± 0.019 and 0.146 ± 0.006; from *o*-xylene, 0.087 ± 0.012 and 0.246 ± 0.020; from *m*-xylene, 0.086 ± 0.011 and 0.319 ± 0.009; from *p*-xylene, 0.225 ± 0.039 and 0.105 ± 0.034; from 1,2,3-trimethylbenzene, 0.058 ± 0.008 and 0.152 ± 0.025; and from 1,2,4-trimethylbenzene, 0.048 ± 0.005 and 0.357 ± 0.017. In addition, a glyoxal yield from benzene of 0.207 ± 0.019, a methylglyoxal yield from 1,3,5-trimethylbenzene of 0.602 ± 0.033, and biacetyl yields from 1,2,3- and 1,2,4-trimethylbenzene of 0.316 ± 0.036 and 0.048 ± 0.009, respectively, were determined. These data are important inputs to chemical models of the NO_x–air photooxidations of these aromatic hydrocarbons.

Introduction

Aromatic hydrocarbons are important constituents of commercial fuels (*1–3*) and of emissions from mobile sources (*1*, *3*). However, despite numerous experimental and computer modeling studies, the reaction pathways occurring during their atmospheric photooxidations are still not well-understood (*4–9*).

Kinetic and environmental chamber studies have shown that under atmospheric conditions the sole loss process of the aromatic hydrocarbons is due to reaction with the hydroxyl radical (*7*, *9–12*). These OH radical reactions have been shown to proceed via two pathways, namely H atom abstraction from the substituent alkyl groups and OH radical addition to the aromatic ring (*7*, *9–12*), as illustrated in eq 1 and 2 for toluene.



The H-atom abstraction route is relatively minor, accounting for ~8% of the overall reaction for toluene (*12*, *13*) and ~2–9% for the xylenes and trimethylbenzenes (*12*). While the subsequent chemistry of the benzyl and substituted benzyl radicals appears to be adequately understood (*7*, *9*, *10*), many uncertainties remain concerning the subsequent chemistry of the OH-aromatic adducts (A) under atmospheric conditions (*7–9*, *12*).

Reaction of the OH-aromatic adducts (i.e., hydroxycyclohexadienyl or methyl-substituted hydroxycyclohexadienyl radicals) with O_2 is expected to lead to the formation of hydroxyaromatics (*7*, *10*, *12*). Indeed the cresol isomers are formed from toluene in ~16% yield (*13*), with *o*-cresol being the dominant isomer (*14*). However, the observation of the α-dicarbonyls glyoxal, methylglyoxal, and biacetyl in significant yields from the methyl-substituted aromatic hydrocarbons (*8*, *13*, *15–19*) and of a variety of other acyclic oxygenated products from toluene (*5*, *6*, *20*), *o*-xylene (*5*), and 1,2,4-trimethylbenzene (*21*)

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shows that ring cleavage is also an important overall reaction pathway.

In this work, in an extension of our recent investigation of the glyoxal and methylglyoxal yields from toluene and *m*- and *p*-xylene (*8*), we have used long-path-length Fourier transform infrared (FT-IR) absorption spectroscopy, long-path-length differential optical absorption spectroscopy (DOAS), and gas chromatography (GC) to determine the yields of the α-dicarbonyls glyoxal, methylglyoxal, and biacetyl from the NO_x–air photooxidations of benzene, toluene, the xylene isomers, and the trimethylbenzene isomers at ~740 torr total pressure of air and 298 ± 2 K.

Experimental Section

The experimental techniques used were essentially identical to those described previously (*8*). NO_x–air photooxidations of the aromatic hydrocarbons were carried out in the SAPRC 5800-L evacuable, Teflon-coated environmental chamber, with radiation being provided by a 25-kW xenon arc (*22*). This environmental chamber is equipped with two sets of multiple-reflection White-type optical systems. One set, on a diametrical axis with a base path of 1.30 m, was interfaced to a Nicolet FT-IR spectrometer. The second set, on a longitudinal axis with a base path of 3.77 m, was interfaced to a differential optical absorption spectrometer.

As in our previous study (*8*), DOAS measurements of glyoxal were carried out using path lengths from 45.2 to 150.8 m, utilizing the wavelength region 430–460 nm. The optimum detection sensitivity for glyoxal was $\sim 3 \times 10^{11}$ molecule cm^{-3} for the maximum path length used (150.8 m). Due to the much weaker spectral features of methylglyoxal (for which the detection sensitivity was $\sim 5 \times 10^{12}$ molecule cm^{-3} at 150 m) its unambiguous detection and measurement by DOAS during these experiments could not be carried out, particularly in the presence of interfering NO_2 absorption bands.

Glyoxal, methylglyoxal, and the aromatic hydrocarbons were monitored by FT-IR absorption spectroscopy simultaneously with the DOAS measurements of glyoxal. For the FT-IR measurements, a path length of 62.9 m was routinely used with a spectral resolution (unapodized) of 1 cm^{-1}. Spectra were recorded by utilizing both a liquid-N_2-cooled HgCdTe detector (600–2000 cm^{-1}) and a liquid-N_2-cooled InSb detector (2000–4000 cm^{-1}). Quantitative analysis was carried out by linear subtraction of a spectrum's absorption bands with the use of calibrated reference spectra of the authentic sample. For the aromatic hydrocarbons the subtraction procedure employed their characteristic absorption bands in both the regions 650–850 cm^{-1} and 2850–3100 cm^{-1}. Glyoxal and methylglyoxal were monitored at their absorptions centered, respectively, at ~2835 and 2829 cm^{-1}. The first step in the analysis of these superimposed absorption bands was the subtraction of the more highly structured band of glyoxal, as verified by the DOAS data, followed by the determination of the residual absorption of methylglyoxal. FT-IR detection sensitivities for glyoxal and methylglyoxal were similar, being $\sim 4 \times 10^{12}$ molecule cm^{-3} at the path length and resolution employed.

Biacetyl was analyzed by gas chromatography with electron capture detection, using a 18 in × 0.25 in. Teflon column of 5% Carbowax 400 on Chromosorb G (80/100 mesh) at 300 K. The detector response was calibrated periodically during this study, and gas samples were diluted as necessary to utilize the linear portion of the calibration curve.

Hydroxyl radicals were generated by the photolysis of methyl nitrite in air at wavelengths ≳300 nm (*7*)

$$CH_3ONO + h\nu \rightarrow CH_3O + NO$$
$$CH_3O + O_2 \rightarrow HCHO + HO_2$$
$$HO_2 + NO \rightarrow OH + NO_2$$

NO was included in the reaction mixtures in order to minimize the formation of O_3 and NO_3 radicals. The initial concentrations of the CH_3ONO–NO–aromatic hydrocarbon–air mixtures were CH_3ONO, $\sim 2.4 \times 10^{14}$ molecule cm^{-3}; NO, $\sim 1.2 \times 10^{14}$ molecule cm^{-3}; aromatic hydrocarbon, $\sim (2.5–5) \times 10^{14}$ molecule cm^{-3}; with approximately 1 atm of synthetic air (80% N_2 + 20% O_2) as the diluent gas.

Each experiment consisted of cumulative, short-period (3–10-min) irradiations, with total irradiation times up to 60 min. DOAS and FT-IR spectra were recorded, and GC samples were taken, between these irradiation periods. This procedure minimized the effect of stray radiation on the DOAS instrument and ensured that all the analyses corresponded to the same extent of reaction. The light intensity in these experiments, as determined from an irradiation of a biacetyl–air mixture, corresponded to a biacetyl photolysis rate of 1.25×10^{-4} s^{-1}.

Results

CH_3ONO–NO–air irradiations of benzene, toluene, *o*-, *m*-, and *p*-xylene, and 1,2,3-, 1,2,4-, and 1,3,5-trimethylbenzene were carried out at 298 K and ~740 torr total pressure of air, with two or three separate experiments being carried out for all but *m*-xylene. The concentrations of the aromatic hydrocarbons, glyoxal, methylglyoxal, and biacetyl as analyzed by FT-IR, DOAS, and GC techniques are given in Tables II–IX. (Tables II–IX are available as supplementary material for this manuscript; see paragraph at end of text regarding supplementary material).

The observed α-dicarbonyl yields had to be corrected for reaction with OH radicals and photolysis (*8*) in order to derive the formation yields of these compounds. The reaction sequence is

$$\text{OH + aromatic} \xrightarrow{\text{NO, O}_2} Y\ \alpha\text{-dicarbonyl} \quad (3)$$
$$\text{OH + } \alpha\text{-dicarbonyl} \rightarrow \text{products} \quad (4)$$
$$\alpha\text{-dicarbonyl} + h\nu \rightarrow \text{products} \quad (5)$$

where reaction 3 is complex (*8*) and Y is the formation yield of the individual α-dicarbonyls from the aromatic hydrocarbon studied. By making the reasonable assumption that the OH radical concentrations were essentially constant over the small irradiation periods, then (*8*)

$$[\text{aromatic}]_{t_2} = [\text{aromatic}]_{t_1} e^{-k_3[\text{OH}](t_2 - t_1)} \quad (\text{I})$$

and

$$[\alpha\text{-dicarbonyl}]_{t_2} = [\alpha\text{-dicarbonyl}]_{t_1} e^{-(k_4[\text{OH}] + k_5)(t_2 - t_1)} + \frac{Y_{t_1 - t_2}[\text{aromatic}]_{t_1} k_3[\text{OH}]}{[(k_4 - k_3)[\text{OH}] + k_5]} [e^{-k_3[\text{OH}](t_2 - t_1)} - e^{-(k_4[\text{OH}] + k_5)(t_2 - t_1)}] \quad (\text{II})$$

where $[\text{aromatic}]_{t_1}$, $[\alpha\text{-dicarbonyl}]_{t_1}$ and $[\text{aromatic}]_{t_2}$, $[\alpha\text{-dicarbonyl}]_{t_2}$ are the aromatic hydrocarbon and α-dicarbonyl concentrations observed at times t_1 and t_2, respectively, and $Y_{t_1 - t_2}$ is the formation yield of the individual α-dicarbonyls over the time period t_1–t_2. Computer calculations showed that eq II yielded negligible (<1%) errors under the experimental conditions utilized in this study. In addition, we have determined (Table III of ref 8) that data obtained from a single long irradiation are indistinguishable from those obtained from several shorter irradiations of the same total duration, thus showing that

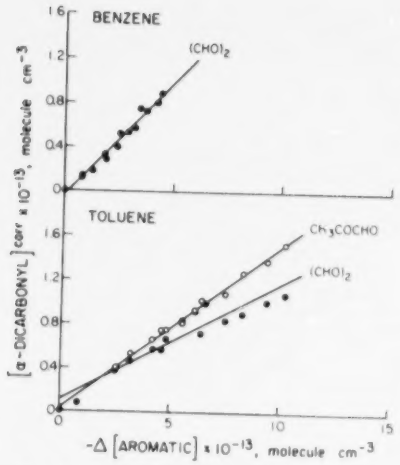

Figure 1. Plots of the glyoxal and methylglyoxal yields (corrected for photolysis and reaction with OH radicals; see text) against the amounts of benzene and toluene consumed.

thermal reactions during the dark analyses periods are of no consequence.

OH radical concentrations were calculated from the aromatic hydrocarbon decays (eq I). Rate constants k_3 and k_4 were taken from the literature (*11*, *23*), with values of k_3 and k_4 (in units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}) of the following: benzene, 1.20; toluene, 6.4; *o*-xylene, 14.6; *m*-xylene, 24.0; *p*-xylene, 14.4; 1,2,3-trimethylbenzene, 33.3; 1,2,4-trimethylbenzene, 40.0; 1,3,5-trimethylbenzene, 62.4; glyoxal, 11.5; methylglyoxal, 17.3; and biacetyl, 0.24. Values of k_4 were obtained by ratioing the previously determined photolysis rates for glyoxal, methylglyoxal, and biacetyl (*23*) with the presently determined photolysis rate of biacetyl, yielding values of k_5 for these experimental conditions of 2.75×10^{-5} s^{-1} and 6.75×10^{-5} s^{-1} for glyoxal and methylglyoxal, respectively. Use of these rate constants together with eq I and II allow $Y_{t_1-t_2}$ to be calculated, and the α-dicarbonyl concentrations, corrected for reaction with OH radicals and photolysis, are then given by

$$[\alpha\text{-dicarbonyl}]_{t_2}^{corr} = [\alpha\text{-dicarbonyl}]_{t_1}^{corr} + Y_{t_1-t_2}([\text{aromatic}]_{t_2} - [\text{aromatic}]_{t_1}) \quad \text{(III)}$$

where $[\alpha\text{-dicarbonyl}]_{t_1}^{corr}$ and $[\alpha\text{-dicarbonyl}]_{t_2}^{corr}$ are the corrected α-dicarbonyl concentrations at times t_1 and t_2, respectively. The correction factors, $[\alpha\text{-dicarbonyl}]_t^{corr}/[\alpha\text{-dicarbonyl}]_t$, were in all cases ≤ 1.67 for glyoxal (for benzene) and ≤ 1.55 for methylglyoxal and were typically ~ 1.2.

The experimental data are given in Tables II–IX together with the corrected values derived from eq I–III. The corrected glyoxal and biacetyl concentrations, $[\alpha\text{-dicarbonyl}]_t^{corr}$, are plotted against the amounts of aromatic hydrocarbon consumed, $-\Delta[\text{aromatic}] = [\text{aromatic}]_t - [\text{aromatic}]_{t_0}$, according to eq III in Figures 1–3. The measurement errors were primarily given by the detection limits of the spectroscopic techniques, such that for glyoxal and methylglyoxal larger relative errors are, or course, associated with the lower yields during the early stage of a reaction. For the aromatic hydrocarbons, at the relatively high concentrations employed, the FT-IR determinations were well within ±1%. In any case, the random scatter of the data plotted in Figures 1–3 shows the extent of these measurement errors in both Δ[aromatic] and $[\alpha\text{-dicarbonyl}]_t^{corr}$. The yields, Y, of glyoxal, methylglyoxal and biacetyl derived from the slopes of such plots by least-squares analyses are listed in Table I.

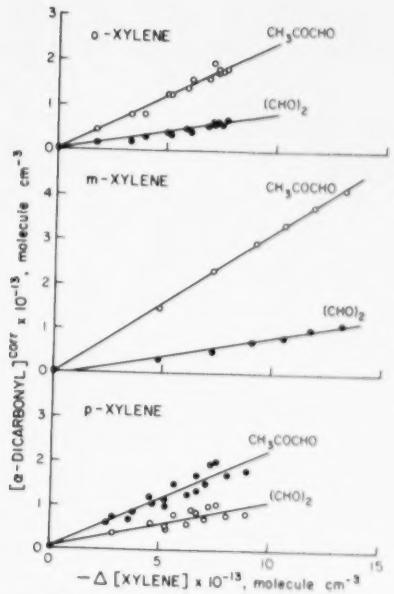

Figure 2. Plots of the glyoxal and methylglyoxal yields (corrected for photolysis and reaction with OH radicals; see text) against the amounts of *o*-, *m*-, and *p*-xylene consumed.

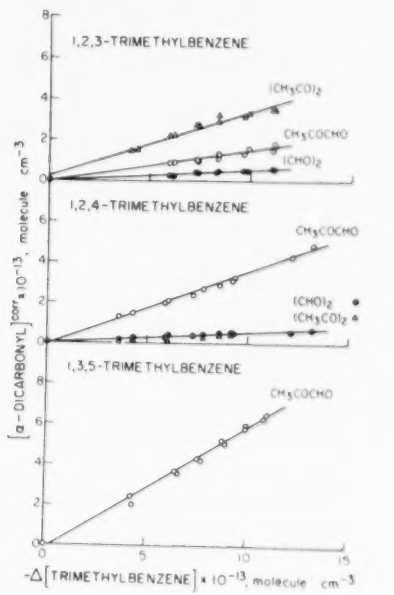

Figure 3. Plots of the glyoxal, methylglyoxal, and biacetyl yields (corrected for photolysis and reaction with OH radicals; see text) against the amounts of 1,2,3-, 1,2,4-, and 1,3,5-trimethylbenzene consumed.

Discussion

The glyoxal and methylglyoxal yields obtained in this work are compared in Table I with our previous glyoxal and methylglyoxal yields (*8*) for toluene and *m*- and *p*-xylene and with other available literature data for toluene, the xylenes, and the trimethylbenzenes. As we have noted previously (*8*), the present α-dicarbonyl yields should be independent (to within $\lesssim$10–15%) of the initial aromatic and NO_x concentrations. This is confirmed by the study of Bandow et al. (*17*), in which the initial NO_x concentrations were varied from 2×10^{13} to 5×10^{13} molecule cm^{-3}, and no dependence of the product yields on the NO_x

Table I. Formation Yields of the α-Dicarbonyls Glyoxal, Methylglyoxal, and Biacetyl from Benzene and the Methyl-Substituted Benzenes, at Room Temperature and Atmospheric Pressure, together with Literature Data

aromatic	α-dicarbonyl yield[a]			ref
	glyoxal	methylglyoxal	biacetyl	
benzene	0.207 ± 0.019			this work
toluene	0.15 ± 0.04	0.14 ± 0.04		17
	0.111 ± 0.013	0.146 ± 0.014		8
	0.105 ± 0.019	0.146 ± 0.006		this work
o-xylene			0.18 ± 0.04	15
			0.260 ± 0.102	16
			0.137 ± 0.016	13
	0.08 ± 0.04	0.23 ± 0.3	0.10 ± 0.02	18
	0.087 ± 0.012	0.246 ± 0.020		this work
m-xylene	0.13 ± 0.03	0.42 ± 0.05		18
	0.104 ± 0.020	0.265 ± 0.035		8
	0.086 ± 0.011	0.319 ± 0.009		this work
p-xylene	0.24 ± 0.02	0.12 ± 0.02		18
	0.120 ± 0.020	0.111 ± 0.015		8
	0.225 ± 0.039	0.105 ± 0.034		this work
1,2,3-trimethylbenzene	0.072 ± 0.001	0.18 ± 0.01	0.45 ± 0.02	19
	0.058 ± 0.008	0.152 ± 0.025	0.316 ± 0.036	this work
1,2,4-trimethylbenzene	0.078 ± 0.005	0.37 ± 0.01	0.11 ± 0.01	19
	0.048 ± 0.005	0.357 ± 0.017	0.048 ± 0.009	this work
1,3,5-trimethylbenzene		0.64 ± 0.03		19
		0.602 ± 0.033		this work

[a] Indicated error limits are 2 standard deviations.

concentration was reported.

It can be seen that the present glyoxal and methylglyoxal yields for toluene, the xylenes, and the trimethylbenzenes are generally in good agreement with those reported by Bandow and co-workers (*17–19*), with the only discrepancies outside of the combined stated error limits occurring for the glyoxal yields from 1,2,3- and 1,2,4-trimethylbenzene. Our glyoxal yield from benzene is the first reported for this aromatic hydrocarbon under conditions reasonably representative of the ambient atmosphere. Furthermore, with the exception of the glyoxal yield from *p*-xylene, our present glyoxal and methylglyoxal yields are in good agreement with those previously determined in this laboratory (*8*). The reasons for the discrepancies between our glyoxal yields from *p*-xylene are not clear, but a significant degree of scatter in the glyoxal yields from run to run for this aromatic hydrocarbon was observed. Our biacetyl yields from 1,2,3- and 1,2,4-trimethylbenzene are ~30–50% lower than those reported by Bandow and Washida (*19*).

Unsaturated 1,4-dicarbonyls have been postulated as counterpart products of the above α-dicarbonyls in the ring cleavage schemes of aromatic hydrocarbons (*7*, *9*, *10*). Thus for example, 3-hexene-2,5-dione and 2-methyl-2-butenedial have been postulated to be the respective coproducts of glyoxal and methylglyoxal from *p*-xylene (*10*). We attempted the detection of 3-hexene-2,5-dione among the irradiation products of *p*-xylene and 1,2,4-trimethylbenzene in the present experiments, since we have previously recorded the FT-IR spectra of both the *trans* and *cis* forms of this 1,4-unsaturated dicarbonyl compound (*24*). Infrared absorptions in the 1100–1400-cm^{-1} region of the residual spectra suggested the possible formation of 3-hexene-2,5-dione from both of these aromatic hydrocarbons, with the absorption features being consistent with the presence of more of the *cis* form than of the *trans* form. Estimates of yields could not be reliably made due to presence of interfering absorptions, among which were those most likely caused by peroxyacyl nitrates (other than peroxyacetyl nitrate). in the case of *p*-xylene the spectral data were not inconsistent with the upper limit yield of *cis*-3-hexene-2,5-dione being similar to that for glyoxal (i.e., ≤25%).

Consistent with our previous conclusions (*8*), it is obvious that the α-dicarbonyl yields do not fully account for the reaction pathways occurring. Thus these α-dicarbonyl yields account for ~20% of the overall reactions for benzene, ~25–30% for toluene, ~30–50% for the xylenes, and ~60% for the trimethylbenzenes if it is assumed that the corresponding unsaturated 1,4-dicarbonyls are formed together with the α-dicarbonyls. However, if the unsaturated 1,4-dicarbonyls are not formed in yields corresponding to the α-dicarbonyl coproducts, then these carbon balances are drastically lower.

The direct reactions of OH radicals with the aromatic hydrocarbons, via H-atom abstraction or, for benzene, H-atom elimination (*12*, *25*) account for ≤10% of the overall OH radical reactions (*12*). Since the reaction pathway giving rise to hydroxyaromatic formation is quantitatively known only for toluene, the extent of presently unrecognized reaction pathways can be estimated only for this aromatic hydrocarbon. As discussed previously (*8*), for toluene only ~50% of the overall reaction pathways can be quantitatively accounted for, although Shepson et al. (*5*) and Dumdei and O'Brien (*6*) have identified a variety of polyfunctional products from the NO_x–air photooxidations of toluene (*5*, *6*) and *o*-xylene (*5*).

Clearly, while the present data set is an important input to chemical computer models concerning the atmospheric chemistry of the aromatic hydrocarbons, work is urgently needed to quantify other products, such as those reported by Shepson et al. (*5*) and Dumdei and O'Brien (*6*), and to further elucidate the reaction pathways occurring during these NO_x–air photooxidations subsequent to the initial OH radical reaction with the parent aromatic hydrocarbons.

Supplementary Material Available

Tables II–IX, listing experimental data for the CH_3ONO–NO–aromatic hydrocarbon–air irradiations (8 pages), will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper or microfiche (105 × 148 mm, 24× reduction, negatives) may be obtained from Microforms Office, American Chemical Society, 1155 16th St., N.W., Washington, DC 20036. Orders must state whether for photocopy or microfiche and give complete

title of article, names of authors, journal issue data, and page numbers Prepayment, check or money order for $13.50 for photocopy ($15.50 foreign) or $6.00 for microfiche ($7.00 foreign), is required and prices are subject to change.

Acknowledgments

We thank William D. Long and Sara M. Aschmann for assistance in conducting these experiments.

Registry No. NO_2, 11104-93-1; OH, 3352-57-6; glyoxal, 107-22-2; methylglyoxal, 78-98-8; biacetyl, 431-03-8; benzene, 71-43-2; toluene, 108-88-3; *o*-xylene, 95-47-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; 1,2,3-trimethylbenzene, 526-73-8; 1,2,4-trimethylbenzene, 95-63-6; 1,3,5-trimethylbenzene, 108-67-8.

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